

^{182}W Mössbauer spectroscopy of heteropolytungstates

Christian G. Bochet, Thérèse Draper, Bernard Bocquet, Michael T. Pope and Alan F. Williams^{*a}

Supplementary material

Characterisation of compounds:

Infrared Spectroscopy (IR)

The infrared spectra were recorded from KBr pellets with a Perkin-Elmer TR-850 or IR-883 spectrophotometer. Wavenumbers are given in cm^{-1} . Abbreviations for the intensities: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder.

H₄SiW₁₂O₄₀ 8 H₂O: DPP (H₂O-AcONa/AcOH 1M): -310 (1), -530 (1), -985 (2). TLC: R_f=0.63. TGA: 5.79% (calcd for 8 H₂O: 5.89%). IR: 1018 (w), 980 (s), 923 (s), 882 (m), 784 (s), 560 (sh), 538 (m), 475 (w), 417 (w), 374 (s), 335 (s), 281 (w), 270 (w), 254 (m).

K₄SiW₁₂O₄₀ 10 H₂O: DPP (H₂O-AcONa/AcOH 1M): -345 (1), -580 (1), -1025 (2). TLC: R_f=0.64. TGA: 5.56% (calcd for 10 H₂O: 5.61%). IR: 1020 (w), 980 (s), 925 (s), 893 (w), 877 (m), 779 (vs), 555 (sh), 539 (m), 477 (w), 419 (w), 378 (s), 282 (m).

[(C₄H₉)₄N]₄SiW₁₂O₄₀: DPP (MeCN/LiClO₄ 0.2M): -700 (1), -960 (1), -1500 (3), -1620 (2). TLC: R_f=0.60. TGA: 26.0% (calcd for 0 H₂O: 26.1%). IR: 2952 (m), 2930 (sh), 2866 (m), 1478 (m), 1455 (m), 1375 (m), 1009 (m), 966 (s), 929 (s), 882 (m), 795 (vs), 552 (sh), 542 (m), 515 (sh), 481 (w), 415 (vw), 386 (s), 339 (m), 280 (w).

H₃PW₁₂O₄₀ 8.5 H₂O: DPP (EtOH/LiClO₄ 1M): -360 (1), -590 (1), -750 (3), -1120 (2). TGA: 7.46% (calcd for 8.5 H₂O 7.65%). IR: 1078 (s), 981 (s), 887 (s), 798 (vs), 595 (w), 523 (m), 480 (sh), 385 (s), 337 (m), 265 (m).

[(C₄H₉)₄N]₃PW₁₂O₄₀: DPP (MeCN/LiClO₄ 0.2M): -395 (1), -655 (1), -905 (2), -1315 (1). TLC: R_f=0.66. TGA: 20.4% (calcd for 0 H₂O: 22.8%). IR: 2960 (m), 2940 (w), 2880 (m), 1470 (m), 1460 (m), 1380 (m), 1080 (s), 1025 (w), 987 (sh), 976 (s), 895 (s), 735 (sh), 657 (w), 596 (w), 522 (m), 387 (s), 375 (sh), 335 (m).

Cs₃PW₁₂O₄₀ 6 H₂O: TGA: 3.24% (calcd for 6 H₂O: 3.19%). IR: 1080 (s), 1000 (sh), 980 (s), 890 (m), 790 (vs), 600 (w), 520 (m), 500 (sh), 380 (s), 330 (m), 268 (m).

Na₃PW₁₂O₄₀ 9 H₂O: DPP (H₂SO₄ 1M): -350 (2), -480 (1), -800 (2). TGA: 7.68% (calcd for 9 H₂O: 7.50%). IR: 1080 (s), 980 (s), 920 (sh), 890 (m), 790 (vs), 600 (w), 530 (m), 380 (s), 330 (m), 340 (m).

K₅AlW₁₂O₄₀ 15 H₂O: DPP (H₂O-AcONa/AcOH 1M): -480 (1), -710 (1), -1010 (4). TLC: R_f=0.48. TGA: 8.22% (calcd for 15 H₂O: 8.09%). IR: 957 (s), 90 (s), 797 (s), 534 (m), 485 (m), 417 (w), 371 (m).

Cs₅AlW₁₂O₄₀ 6 H₂O: DPP (H₂SO₄ 0.1M/Na₂SO₄ 0.9M): -445(1), -620 (1), -770 (1). TLC: R_f=0.58. TGA: 3.23% (calcd for 6 H₂O: 2.96%). IR: 954 (s), 873 (s), 800 (s), 757, 537 (m), 485 (m), 472 (m), 374 (s).

[(C₄H₉)₄N]₄HAlW₁₂O₄₀ 3 H₂O: TLC: R_f=0.58. TGA: 27.3% (calcd for 3 H₂O: 27.3%). IR: 990 (sh), 956 (s), 910 (sh), 878 (s), 800 (vs), 750 (sh), 540 (w), 485 (w), 475 (sh), 400 (sh), 380 (m), 355 (sh), 328 (sh).

H₅BW₁₂O₄₀ 15 H₂O: DPP (H₂O -AcOH/AcONa 1M): -380 (1), -595 (1), -1045 (2). TGA: 10.14% (calcd for 15 H₂O:10.06%).

K₅BW₁₂O₄₀ 11 H₂O : DPP (H₂O -AcOH/AcONa 1M): -540 (1), -770 (1). TLC: Rf=0.63. TGA: 6.23% (calcd for 11 H₂O: 6.09%). IR: 1000 (m), 957 (s), 905 (s), 800 (vs), 520 (sh), 510 (m), 480 (sh), 423 (w), 380 (m), 335 (m), 285.

[(C₄H₉)₄N]₃AsW₁₂O₄₀ : DPP (MeCN/LiClO₄ 0.2M): -425 (1), -680 (1), -950 (2), -1320 (1). TLC: Rf=0.66. TGA: 23.53% (calcd: 23.72%). IR: 2980 (m), 2930 (sh), 2870 (m), 1460 (m), 1380 (m), 983 (s), 912 (s), 873 (m), 793 (vs), 735 (sh), 680 (w), 525 (m), 470 (m), 420 (w), 381 (s), 358 (sh), 325 (w).

Cs₃AsW₁₂O₄₀ 10 H₂O : DPP (H₂O -AcOH/AcONa 1M): -540 (1), -840 (2), -910 (2). TGA: 5.32% (calcd for 10 H₂O: 5.15%). IR: 968 (s), 890 (s), 865 (sh), 792 (s), 740 (sh), 620 (sh), 520 (m), 472 (m), 466 (s), 418 (m), 322 (w), 301 (w).

[(C₄H₉)₄N]₄HFeW₁₂O₄₀ 4 H₂O : TLC: Rf=0.59. TGA: 27.6% (calcd for 4 H₂O: 27.5%). IR: 952 (s), 915 (sh), 872 (s), 775 (s), 725 (sh), 680 (vw), 580-500, 448 (s), 372 (s).

[(C₄H₉)₄N]₄H₂CoW₁₂O₄₀ 6 H₂O : DPP (MeCN/LiClO₄ 0.2M): -650 (1), -900 (1), -1350 (1). TLC: Rf=0.40. TGA: 28.2% (calcd for 6 H₂O: 28.3%). IR: 2960 (m), 2920 (m), 2860 (m), 1480 (m), 1455 (sh), 1380 (m), 943 (s), 887 (s), 786 (vs), 682 (sh), 565, 445 (s), 366 (s). UV-Vis (MeCN): 17718 (sh, 104.5), 16824 (sh, 183.6), 16000 (210.45), 15576 (sh, 194).

[(C₄H₉)₄N]₄GeW₁₂O₄₀ : DPP (MeCN/LiClO₄ 0.2M): -675 (1), -900 (1), -1175 (1). TLC: Rf=0.61. TGA: 25.6% (calcd for 0 H₂O: 25.8%). IR: 2958 (m), 2930 (sh), 2863 (m), 1480 (m), 1455 (m), 1378 (m), 990 (sh), 962 (s), 880 (s), 830 (m), 780 (s), 530 (w), 464 (m), 410 (vw), 380 (s).

[(C₄H₉)₄N]₄H₂ZnW₁₂O₄₀ 3 H₂O : DPP: -470 (1), -650 (4), -980 (1). TLC: Rf=0.35. TGA: 27.3% (calcd for 3 H₂O: 27.3%). IR: 2960 (m), 2920 (sh), 2860 (m), 1460 (m), 1375 (m), 970 (sh), 943 (s), 875 (s), 760 (vs), 680 (w), 446 (m), 365 (m).

K₆H₂W₁₂O₄₀ 2 H₂O : DPP (H₂O -AcOH/AcONa 1M): -700 (1), -780 (1), -960 (2), -1140 (4). TLC: Rf=0.33. IR: 1396 (m), 1354 (w), 1252 (s), 969 (m), 950 (s), 876 (s), 762 (vs), 609 (m), 420 (s), 375 (s), 325 (w), 282 (m).